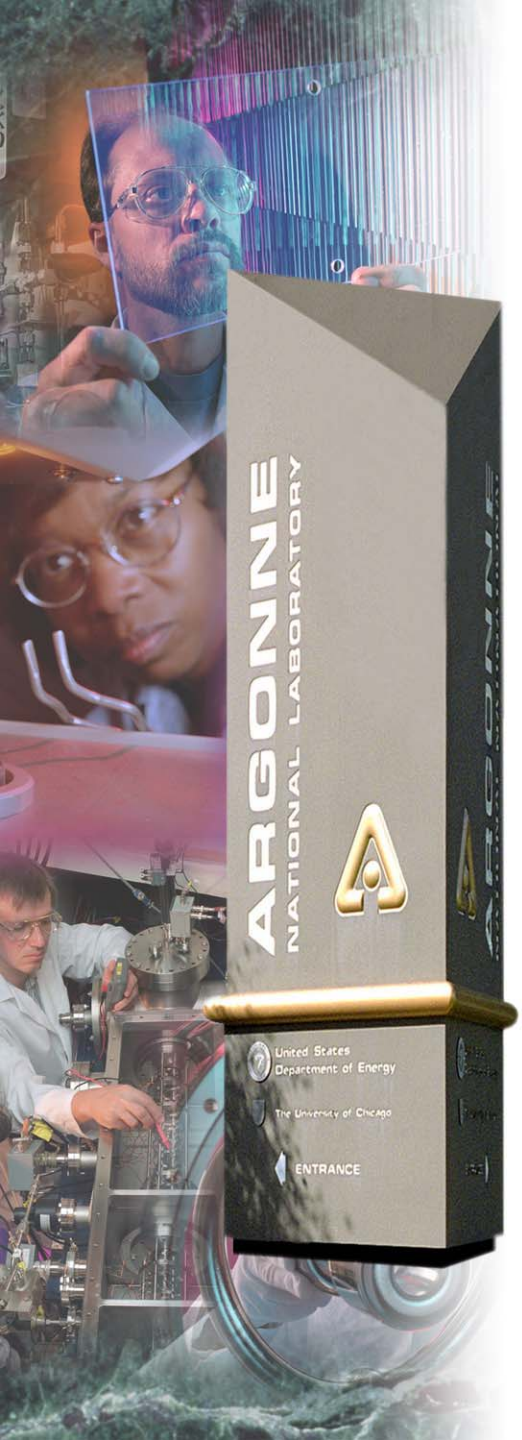

Lithium-based mixed surface experiments

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Plasma Facing Components (PFC) Meeting
Princeton, NJ
May 9-11, 2005

Argonne National Laboratory

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Office of Science
U.S. Department of Energy

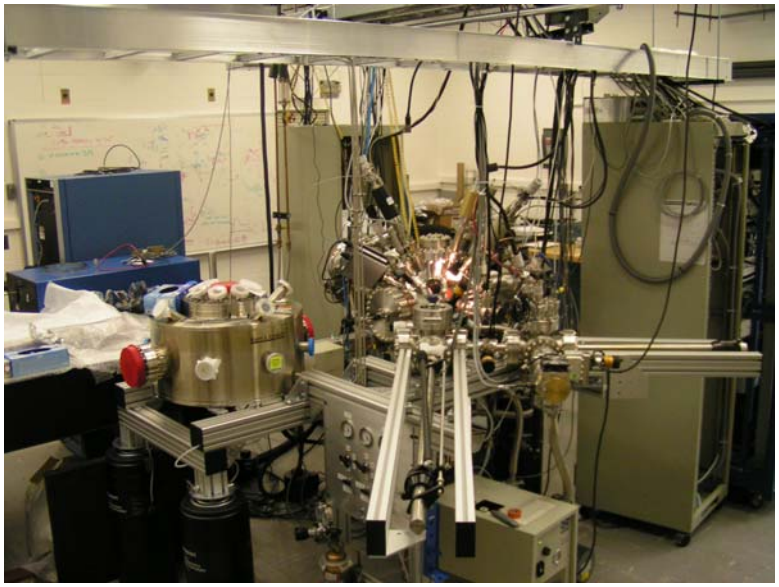
Outline of talk

- Lithium-based mixed surface studies in *IMPACT*: overview
- Description of *IMPACT* experiment at Argonne
- Hydrocarbon evolution on non-lithiated graphitic surfaces under D^+ bombardment
- Hydrocarbon evolution on lithiated graphitic surfaces under D^+ bombardment
- Erosion from lithium thin-films on stainless steel
- Summary
- Future work

Motivation of Li thin-film coatings studies in IMPACT

- **Lithium thin-film coatings on ATJ graphite tiles are proposed as Phase 1 of Module A plan in NSTX.**
  - Phase 2 of Module A will consist of W or Mo-coated surfaces to be used with lithium
  - Solid lithium coatings are also being used in CDX-U (LTX).
- **Experiments at Argonne and Sandia/Livermore study thin-film lithium-based systems with respect to:**
  - Study of lithium evolution on graphite surfaces and boron-treated graphite surfaces (polished and unpolished)
  - Study of hydrocarbon evolution under low-energy D bombardment on lithiated and non-lithiated graphite surfaces.
  - Bombardment-induced sputtering (He^+, D^+, etc…) of lithium-treated graphite and alternate substrates
  - Evolution of lithium on Mo, W, and SS substrates

IMPACT (Interactions of Materials with charged Particles and Components Testing) Experiment at Argonne



- **The IMPACT experiment is designed to study multi-functional and multi-component surfaces and interfaces under extreme particle irradiation conditions.**
- **IMPACT consists of in-situ metrology obtaining time-dependent measurement of: surface evolution, surface erosion and eroded particle energy distributions while under energetic particle irradiation.**

IMPACT in-situ metrology

EUV source: EUPS

Multiple ion sources: ion-induced mechanisms

Surface analysis: **LEISS, DRS**

Electron source: AES

Inficon Quadrupole mass spectrometer (QMS)

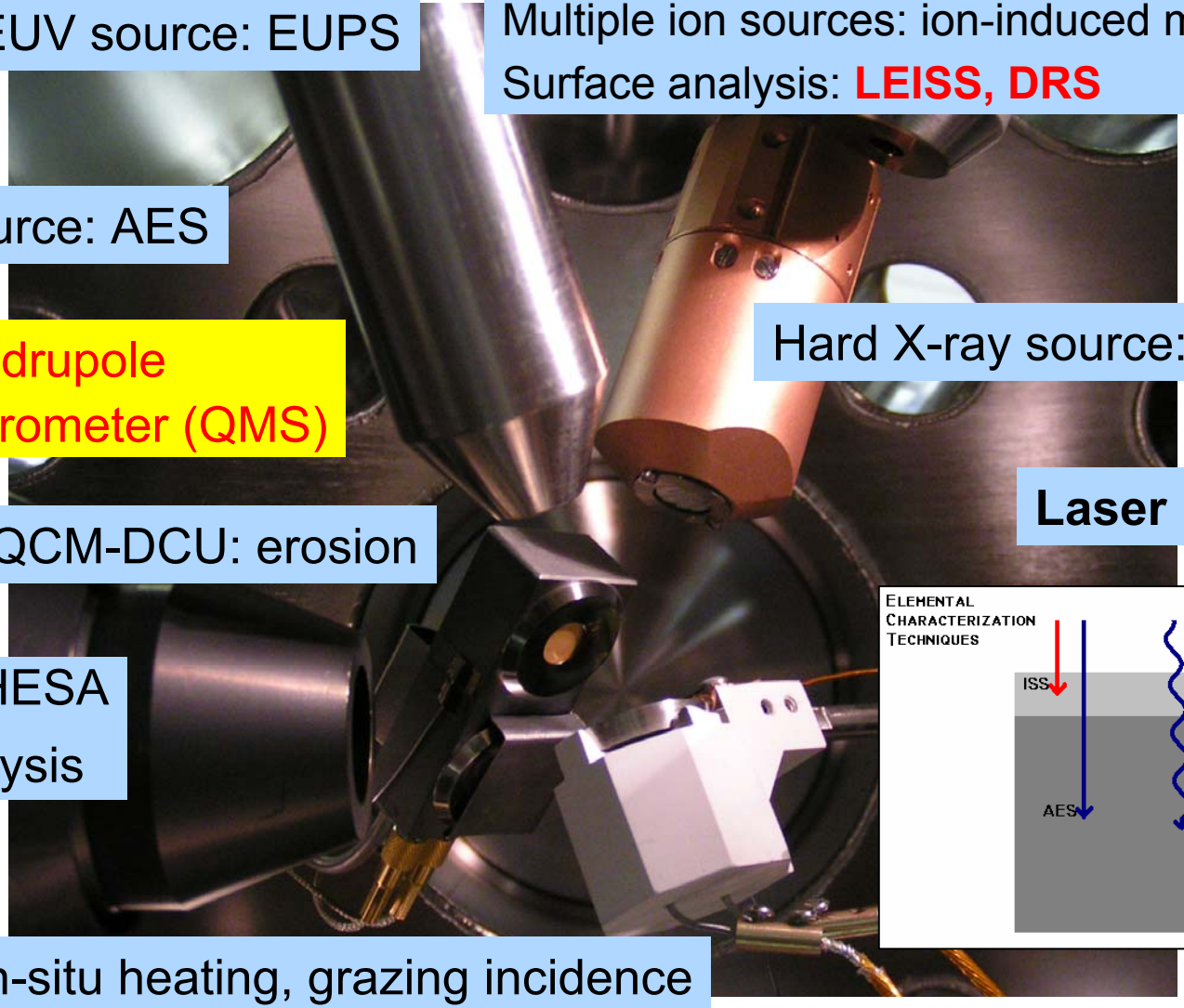
Hard X-ray source: XPS

Laser PI-SNMS

QCM-DCU: erosion

PHOIBOS HESA

Energy analysis



In-situ heating, grazing incidence

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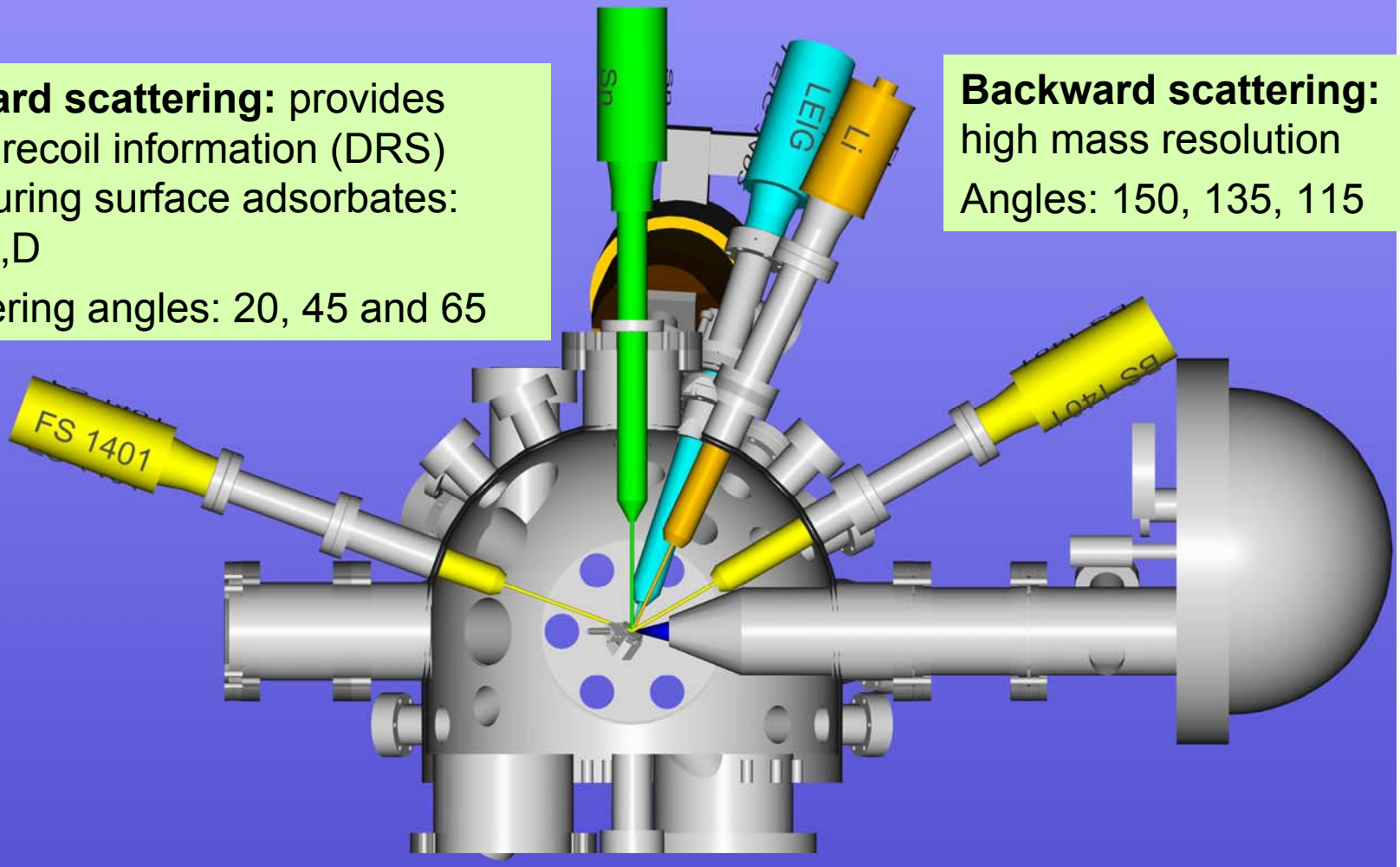
Complete diagnosis of a multi-component surface under irradiation

Forward scattering: provides direct recoil information (DRS) measuring surface adsorbates: e.g. H,D

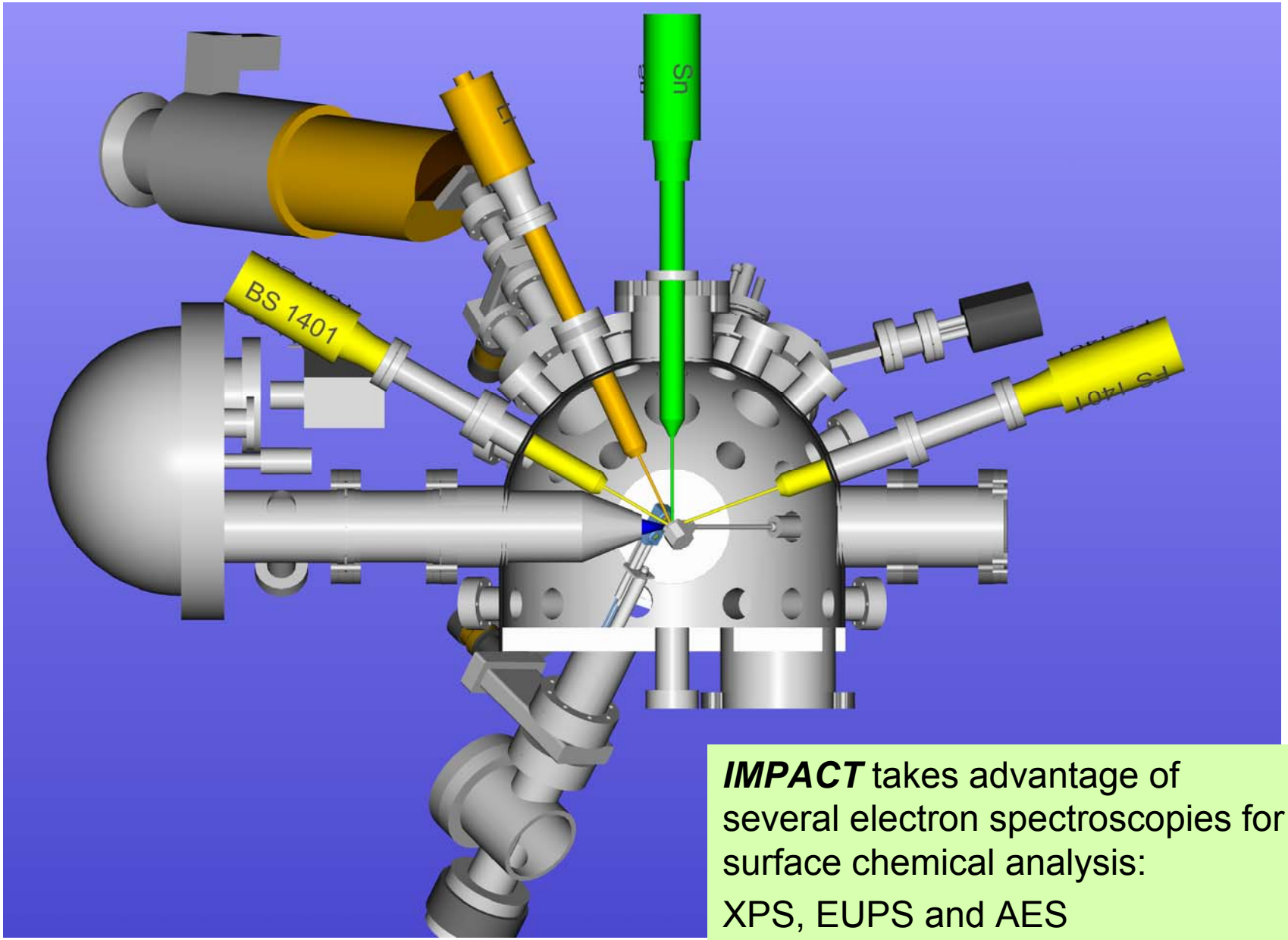
Scattering angles: 20, 45 and 65

Backward scattering: high mass resolution

Angles: 150, 135, 115



- Multi-ion source system to provide simultaneous forward and backward scattering on multi-component surfaces. **Two additional ion sources:** 1) high-intensity low-energy gun 2) Li alkali-metal ion gun



IMPACT takes advantage of several electron spectroscopies for surface chemical analysis:

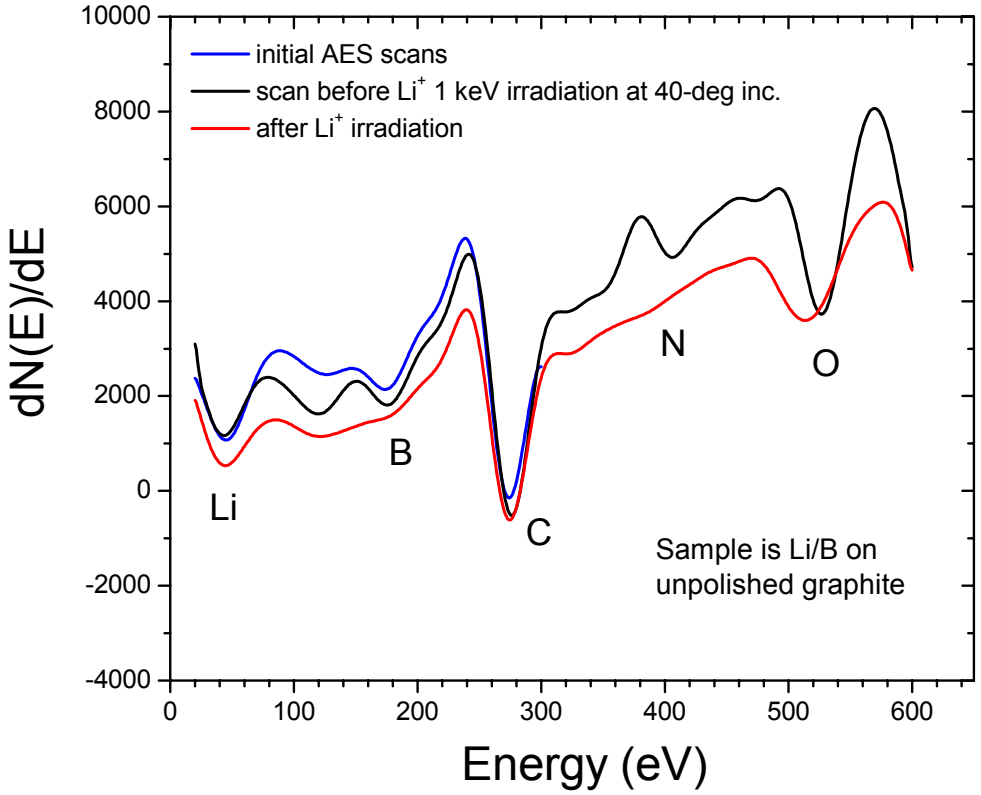
XPS, EUPS and AES

Summary of work in IMPACT on Li-covered surfaces

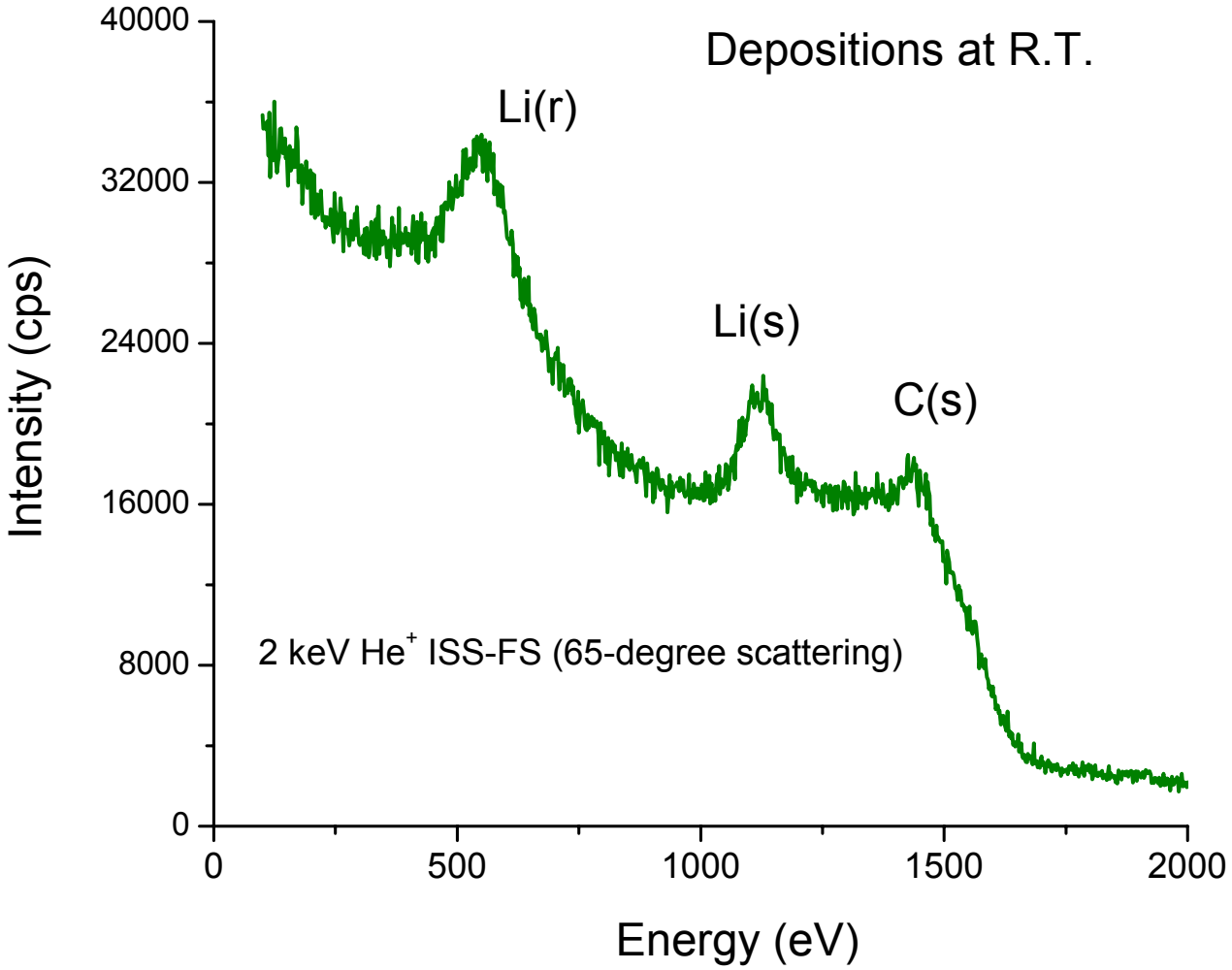
- Li-treated surface consist of various species that make the study of lithiated systems quite complex.
- This is mainly due to lithium's high reactivity with H,D,O and N.
- We're interested in understanding what a mixed surface consisting of e.g. Li, B and C does to net erosion of material (i.e. partial sputtering of Li vs B vs C)
- We also would like to know the role Li and impurities have on hydrocarbon formation when Li/C surfaces are bombarded with D
- We want to know how Li thin-films on SS, Mo and W behave. Are sputtering levels similar to pure liquid Li surfaces? What is the surface coverage of Li as function of temp? Effect on D recycling?

Li^+ bombardment on Li/B graphite

- **The presence of boron does not prevent Li diffusion into graphite (in both polished and unpolished forms)**
- **Oxygen is present with Li at all times (before and after Li^+ irradiation). Li^+ irradiation removes nitrogen impurity and induces Li segregation to the surface of the B/C system.**

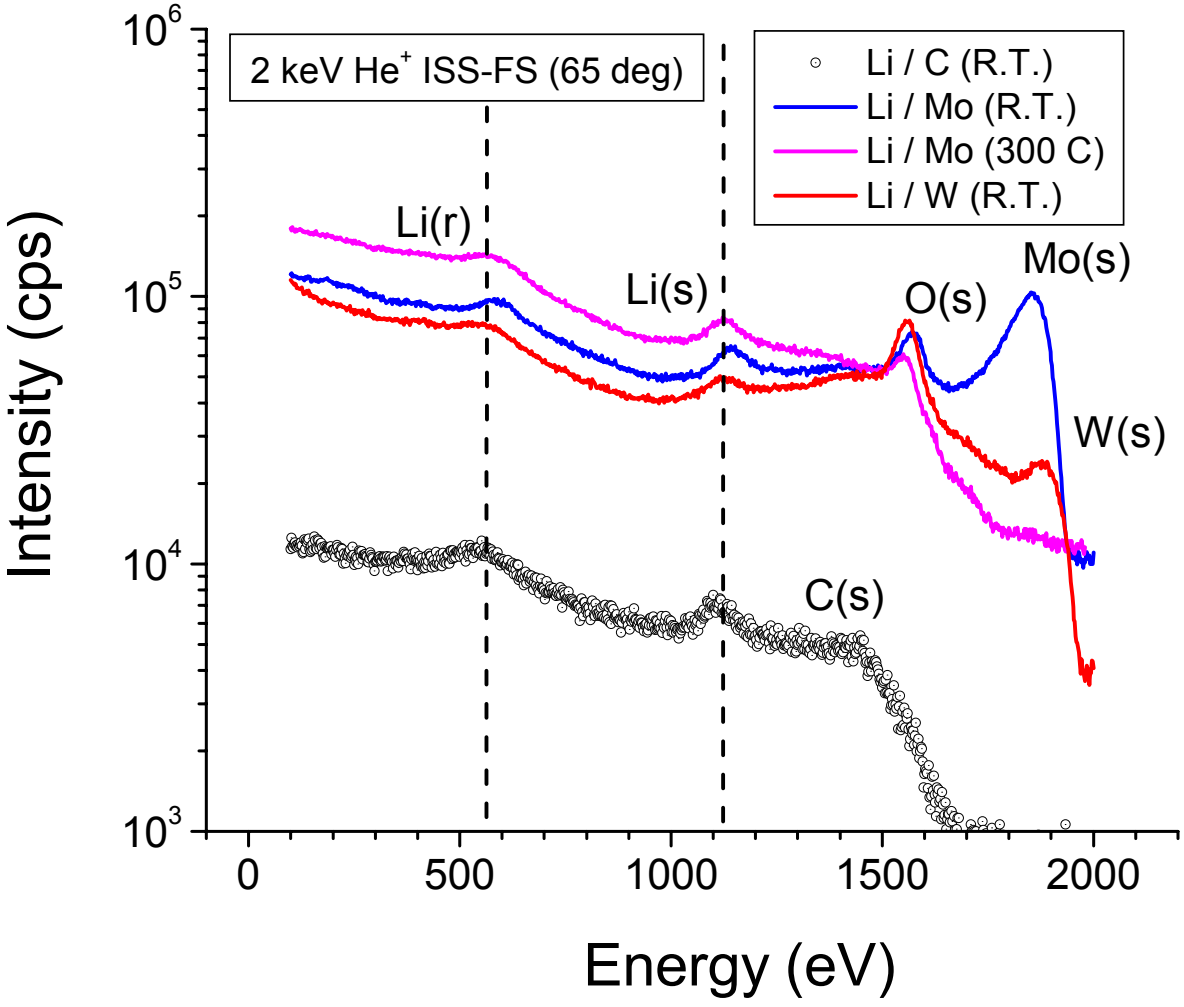


In-situ evaporation of Li on C

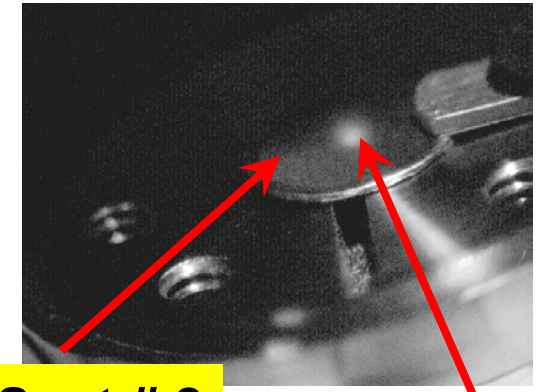


Real time measurement of Li deposition on ATJ graphite

Comparison to Li evaporation on other metal substrates (W, Mo)

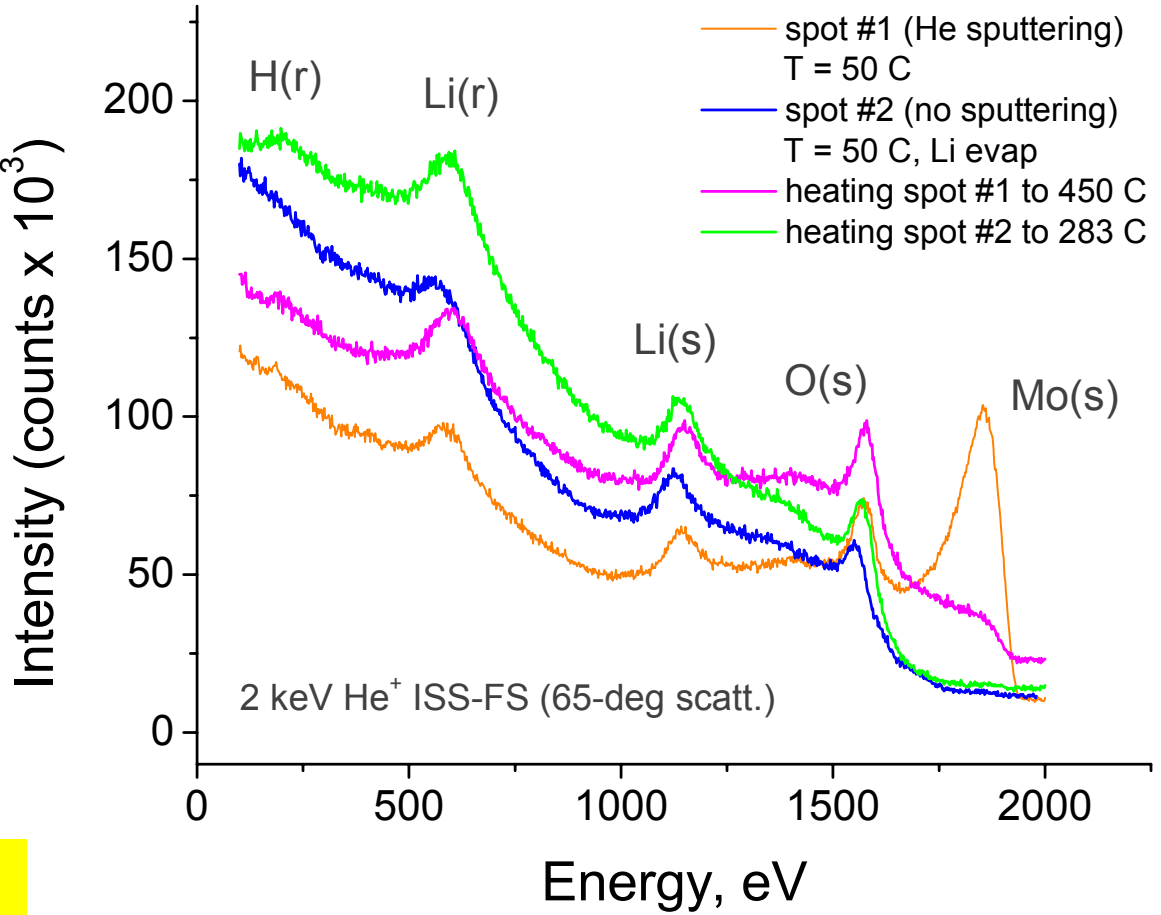


- Li and O are the dominant species on the surface of Mo
- Li surface is recovered at high temps after He^+ irradiation



Spot # 2

Spot # 1



Interactions of D bombardment with lithiated ATJ graphite samples

- **Determine how the deuterium-carbon interactions are modified by the presence of Li in ATJ graphite**
- **Some of the aspects relevant to D/graphite interactions influenced by the presence of Li are:**
  - Physical sputtering vs Chemical erosion, D chemisorption, D backscattering (reflection), D implantation, etc…
- **Hydrocarbon emissions during bombardment of graphite with low-energy D^+ were observed and monitored with an Inficon Transpector quadrupole mass spectrometer (QMS)**
- **Qualitative results regarding hydrocarbon emissions are presented here, future work will quantify these results**
- **Methodology for quantitative analysis will be outlined and applied to this and other data in the near future**

Identification and quantification of gases from QMS-RGA data

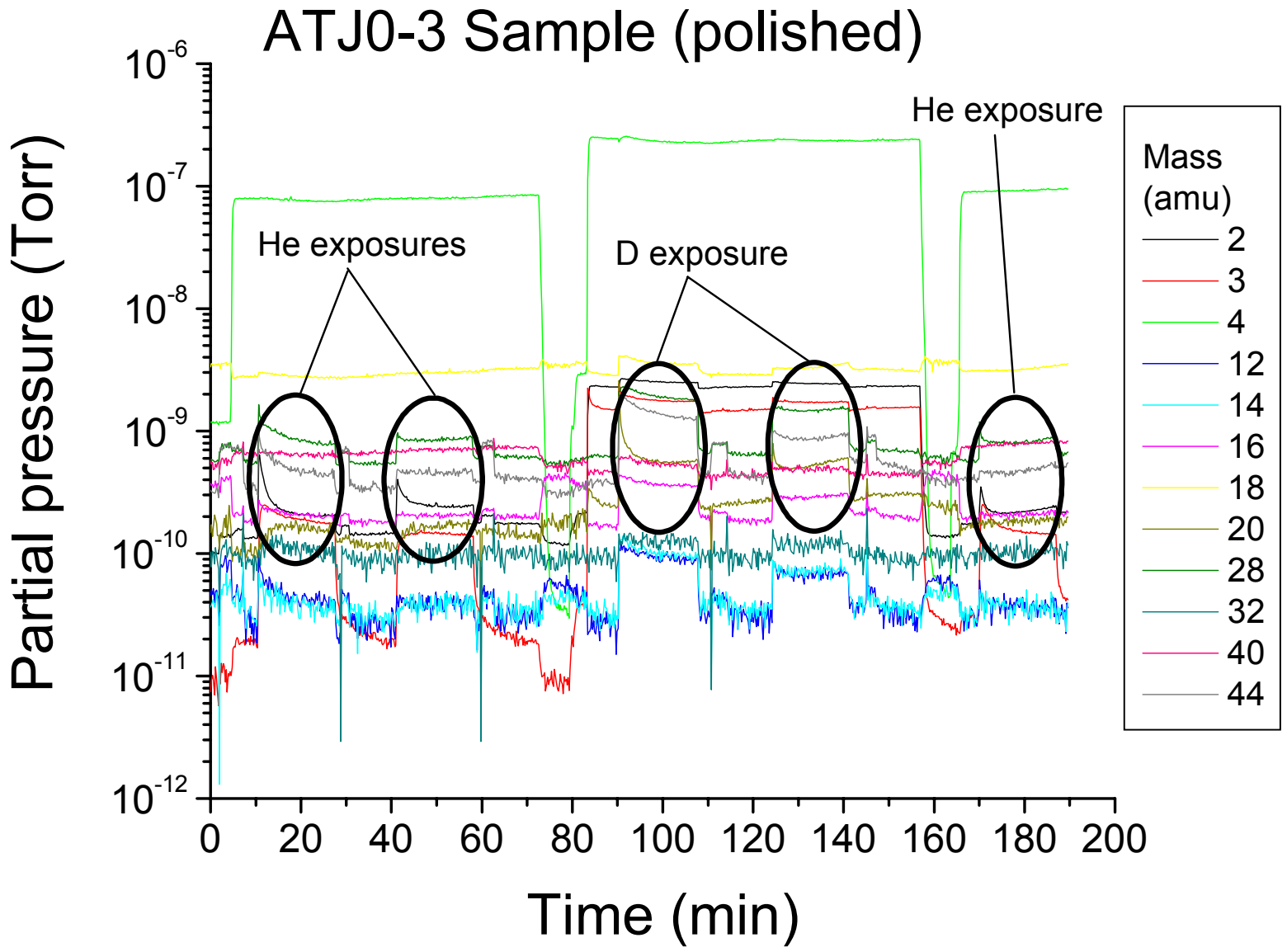
- Molecules ionized in an RGA "crack" into fragments with different masses and/or charges
- Each fragment will have a certain abundance
- Intensities are typically determined from experimental measurements or are widely known in the literature
- Usually the relative abundances for the fragments are normalized to the intensity of the main fragment, so the strongest peak is assigned 100% intensity
- This is done so that the signal from the main fragment equals the partial pressure
- Typical problems: overlapping lines (CO and N_2), total pressure calibration, preferential consumption of a fragment, etc.
- The following tables present relative intensities for hydrocarbons from NIST (assumed the same for deuterated HC's as for protium)

Deuterated HC cracking patterns

Mass	Fragment	CD_4	C_2D_4	C_2D_6	C_2D_2
12	C			> 1	
14	CD	11		1	3
16	CD_2	20		3	
18	CD_3	89		4	
20	CD_4	100			
24	C_2		3		5
26	C_2D		8	4	19
28	C_2D_2		53	23	100
30	C_2D_3		62	33	
32	C_2D_4		100	100	
34	C_2D_5		2	21	
36	C_2D_6			27	

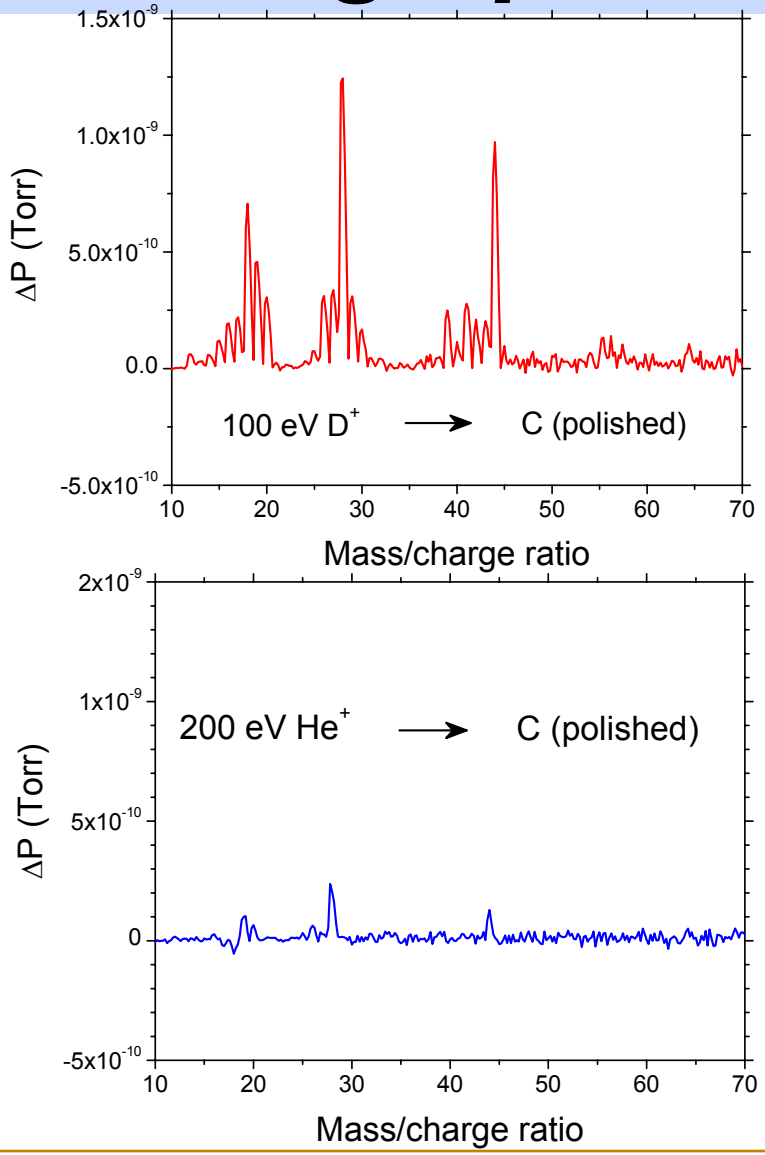
Experimental Setup of Li/C work

- **Four samples studied at room temperature:**
  - Two were polished and unpolished ATJ graphite
  - The other two, evaporated with 100-500 nm of Li with the same surface morphologies
- **Evaporation of Li on graphite done *ex-situ* from main chamber and sample is transported and loaded in-vacuo**
- **Polished graphite samples were not annealed and surface characterization showed H,O peaks**
- **Samples bombarded with low energy D^+, 50 and 125 eV/amu (100 and 250 eV D^+ beam) at 40-degree incidence. Ion beam assumed to consist mainly of D^+ species; however measurements are underway to assess the exact molecular make-up of the beam. Therefore, corrections to both the energy and flux may be needed.**
- **A Inficon quadrupole mass spectrometer used for tracking of hydrocarbon evolution (calibrated with known sources)**

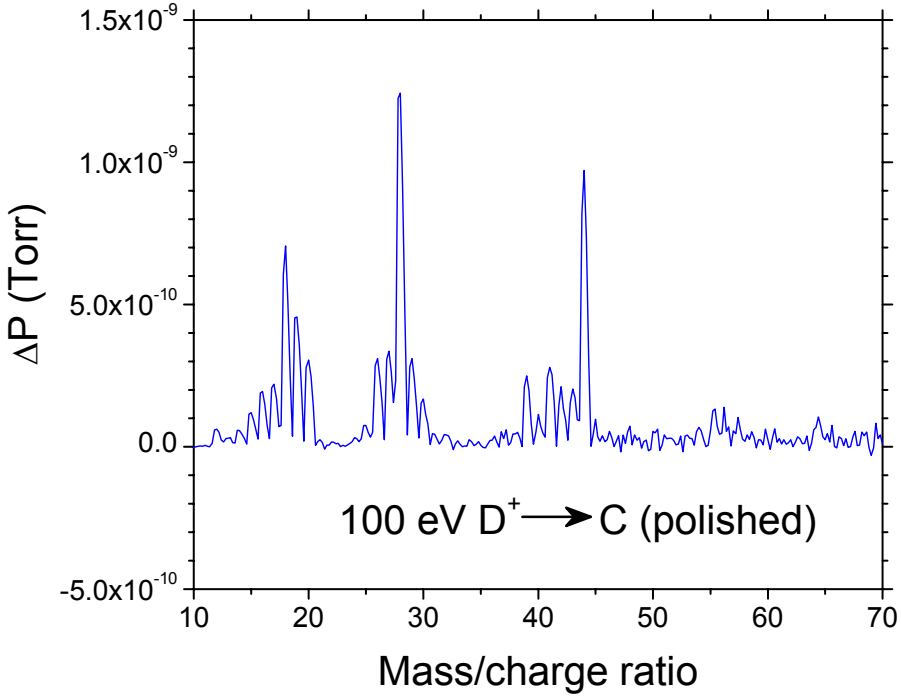

ATJ0-3 Sample (polished)
Partial pressure (Torr)
10-6
10-7
10-8
10-9
10-10
10-11
10-12
He exposures
D exposure
He exposure
Mass (amu)
2
3
4
12
14
16
18
20
28
32
40
44
0
20
40
60
80
100
120
140
160
180
200
Time (min)

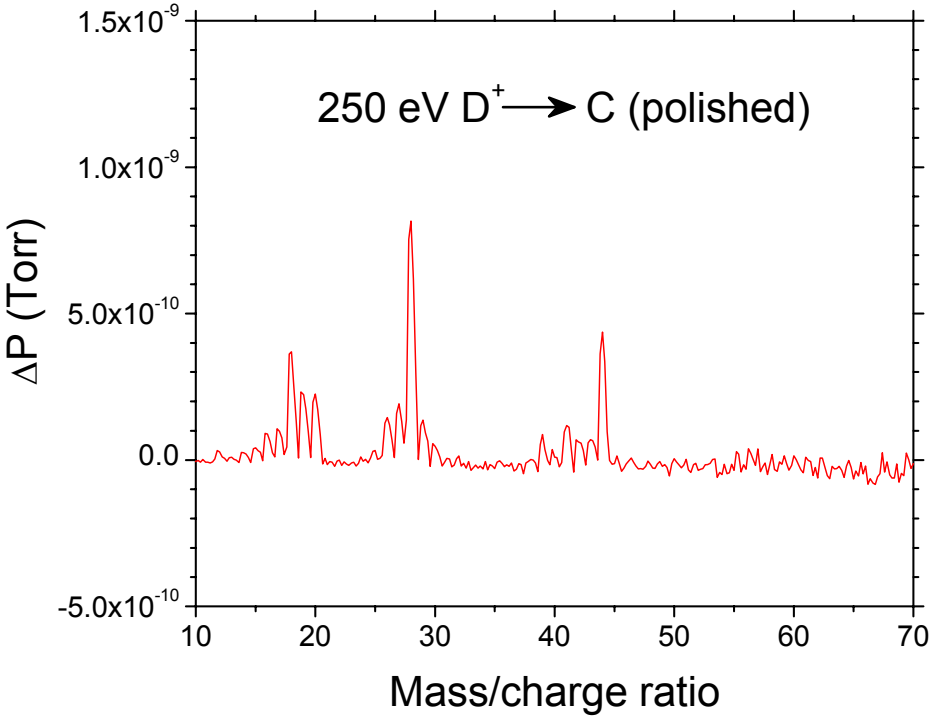
D^+ vs He^+ irradiation of graphite

- ΔP is the partial pressure with a steady-state background spectrum subtracted.
- 50 eV/amu bombardment of C sample with D and He, with the same ion current
- Hydrocarbon peaks go up significantly for the case of D bombardment
- Emission of 18, 28, and 44 is measured under He bombardment (H_2O, CO, N_2 and CO_2)



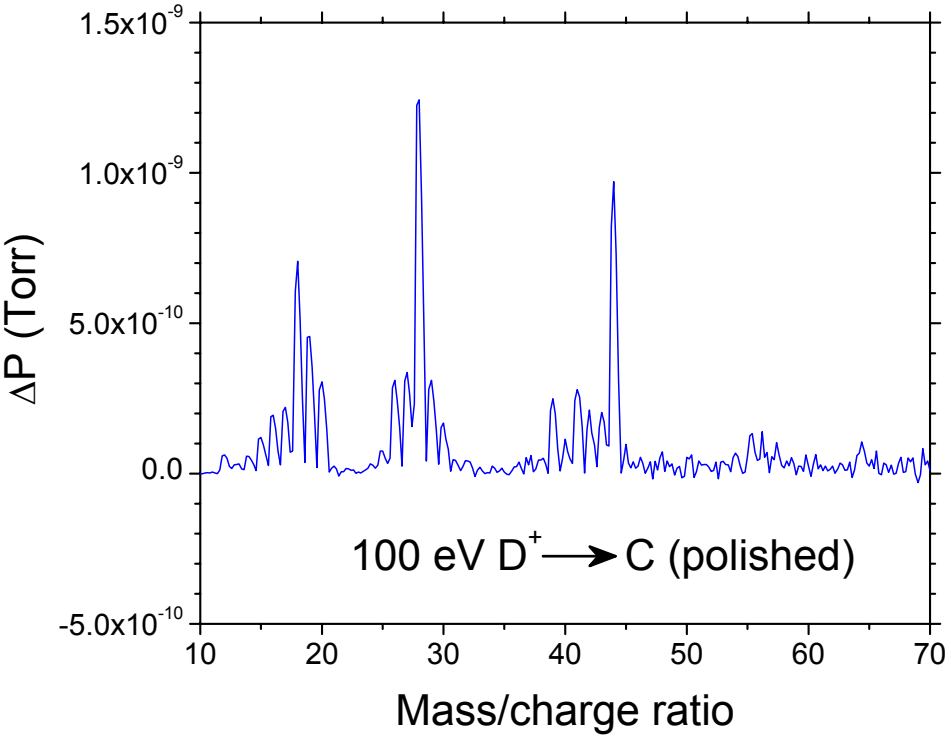
Effect of energy deposition

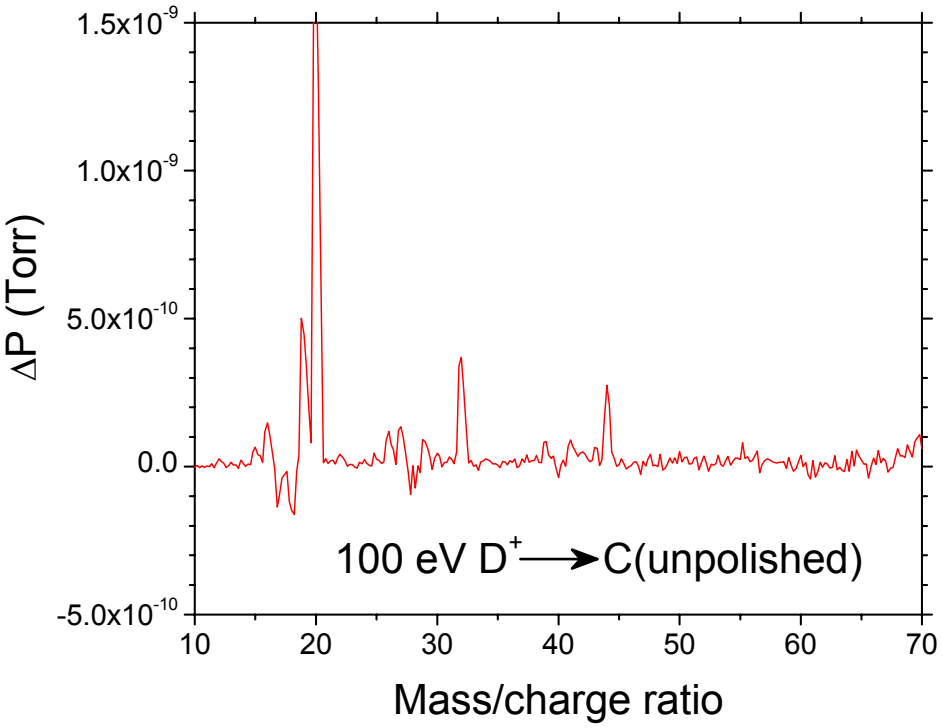




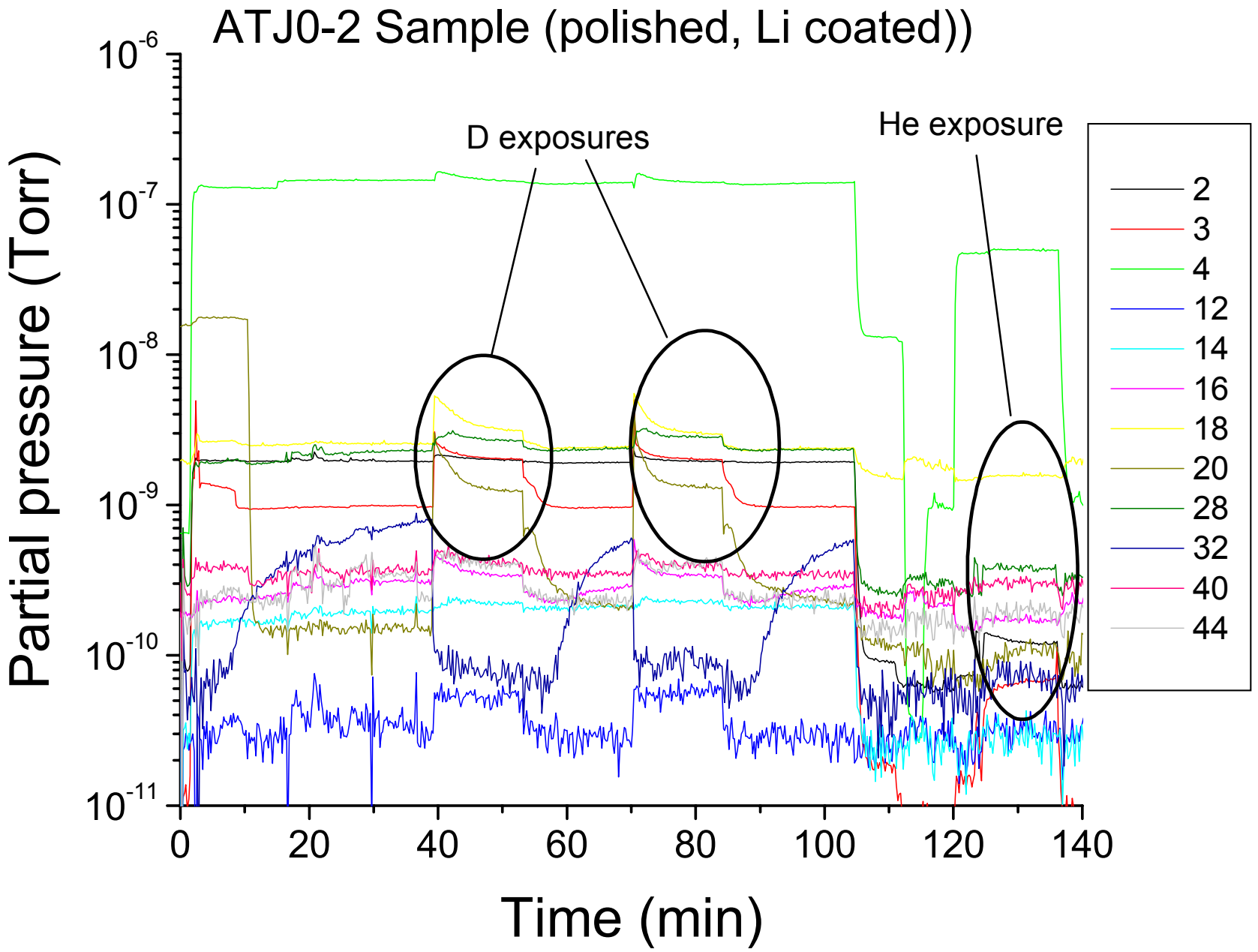
- **Two cases: 50 eV/amu and 125 eV/amu on polished ATJ graphite**
- **No change in relative ratios of the hydrocarbons at each incident D energy**
- **Spectra are very similar, higher methane ejection at lower impact energy (in agreement with B.V. Mech, A.A. Haasz, J.W. Davis, JNM 255 (1998) 153)**

Effect of surface morphology





- More emission of mass 20 (D_2O + CD_4) in the unpolished sample
- Little emission of C_2 and C_3 HC's on the unpolished sample
- O_2 and CO_2 emission from unpolished substrate, but no CO emission



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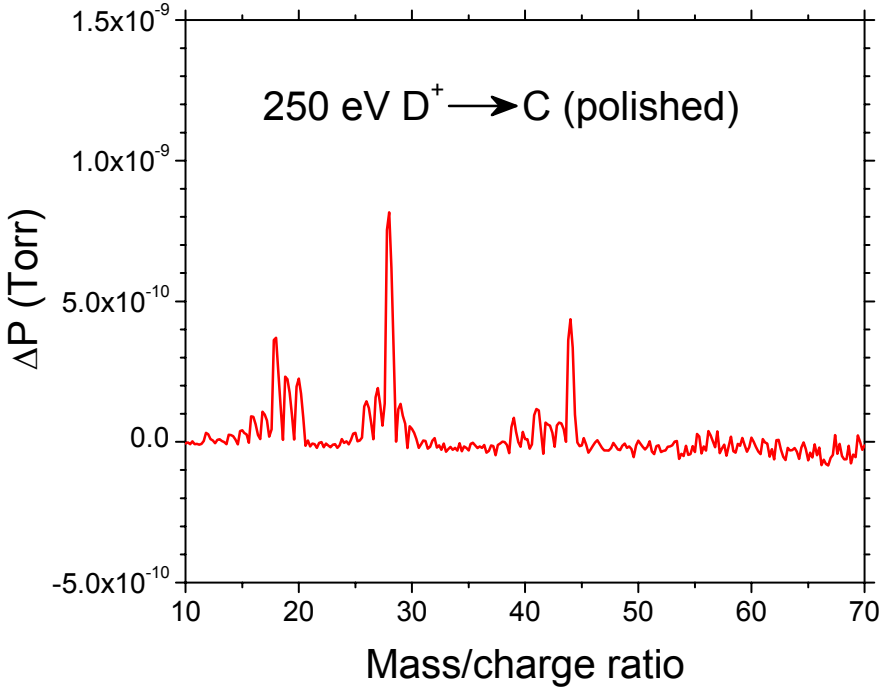
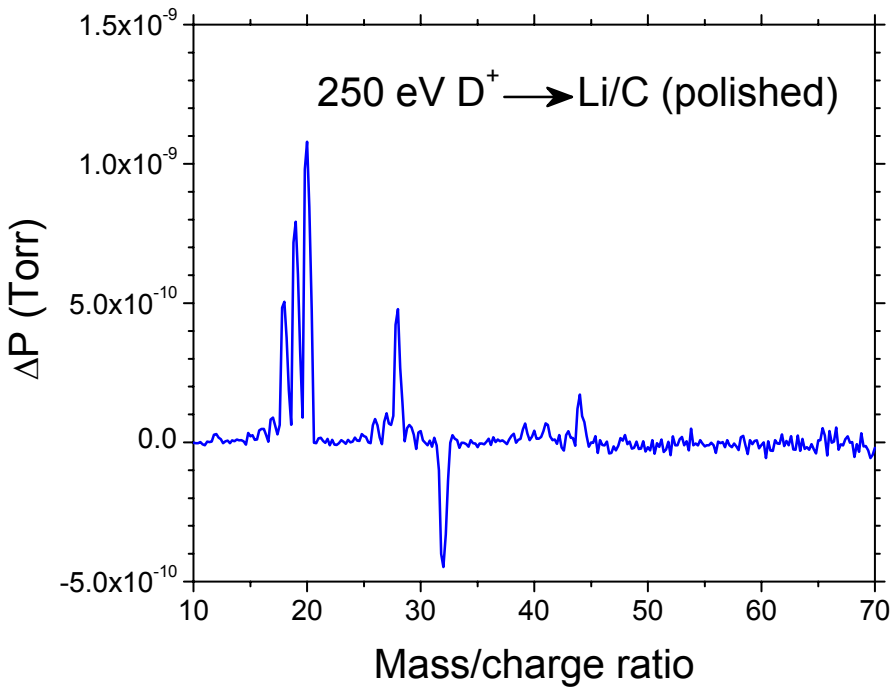
Now what happens if we add lithium

Comparison between C and Li/C

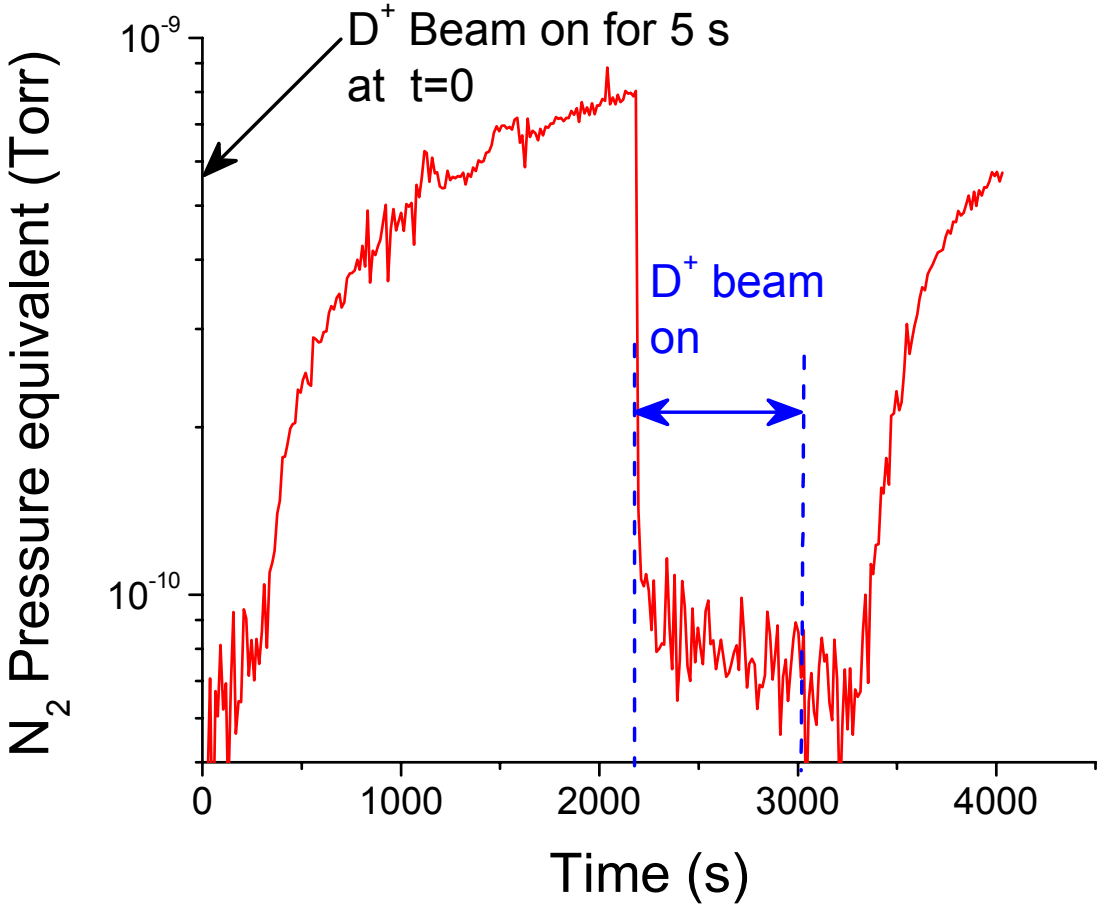




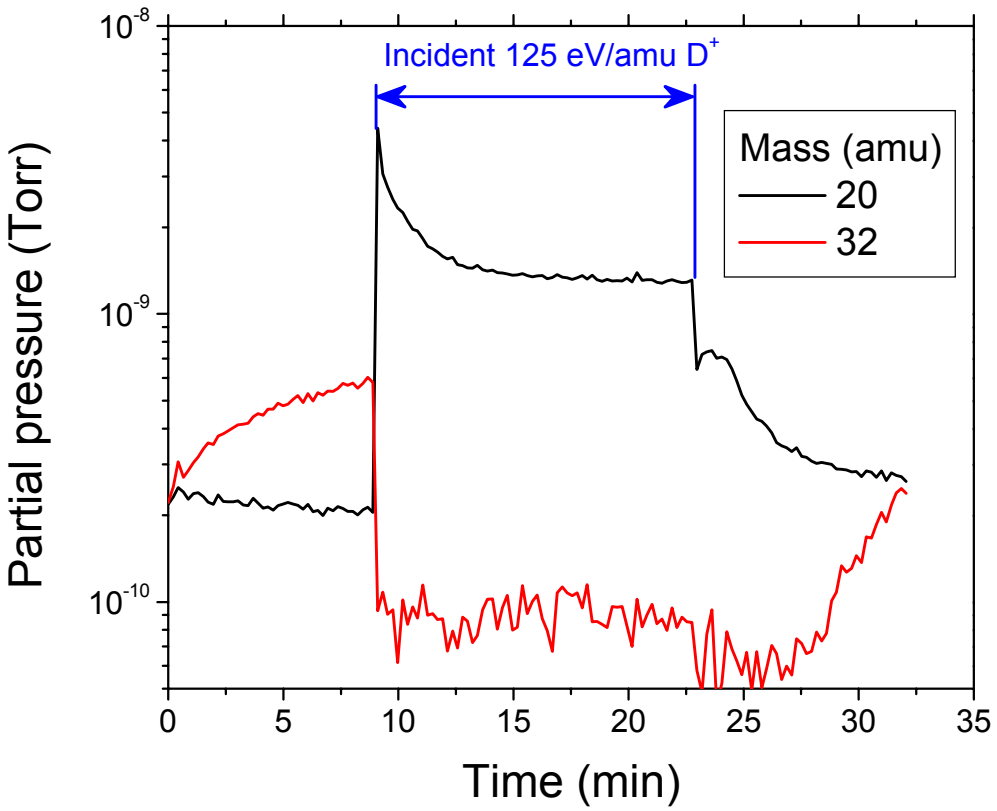
- **Group at around mass 20 seems to increase for the Li coated sample**
- **Shape of the group resembles water breakdown**
- **Could we be forming D_20? or is this peak methane formation?**
- **Suppression of the mass 32 peak seems to suggest the possibility that heavy water formation is more likely, and methane emission is suppressed.**

Results from C/Li samples

- Interesting behavior of mass 32
- Mass 32 suppression DURING D^+ irradiation
- Initial D exposure only for short 5-10 sec
- Delayed increase after D irradiation (even with very short time bombardment!)
- Desorption of O_2 from Li surface?
- This phenomenon is observed only with lithiated ATJ graphite samples



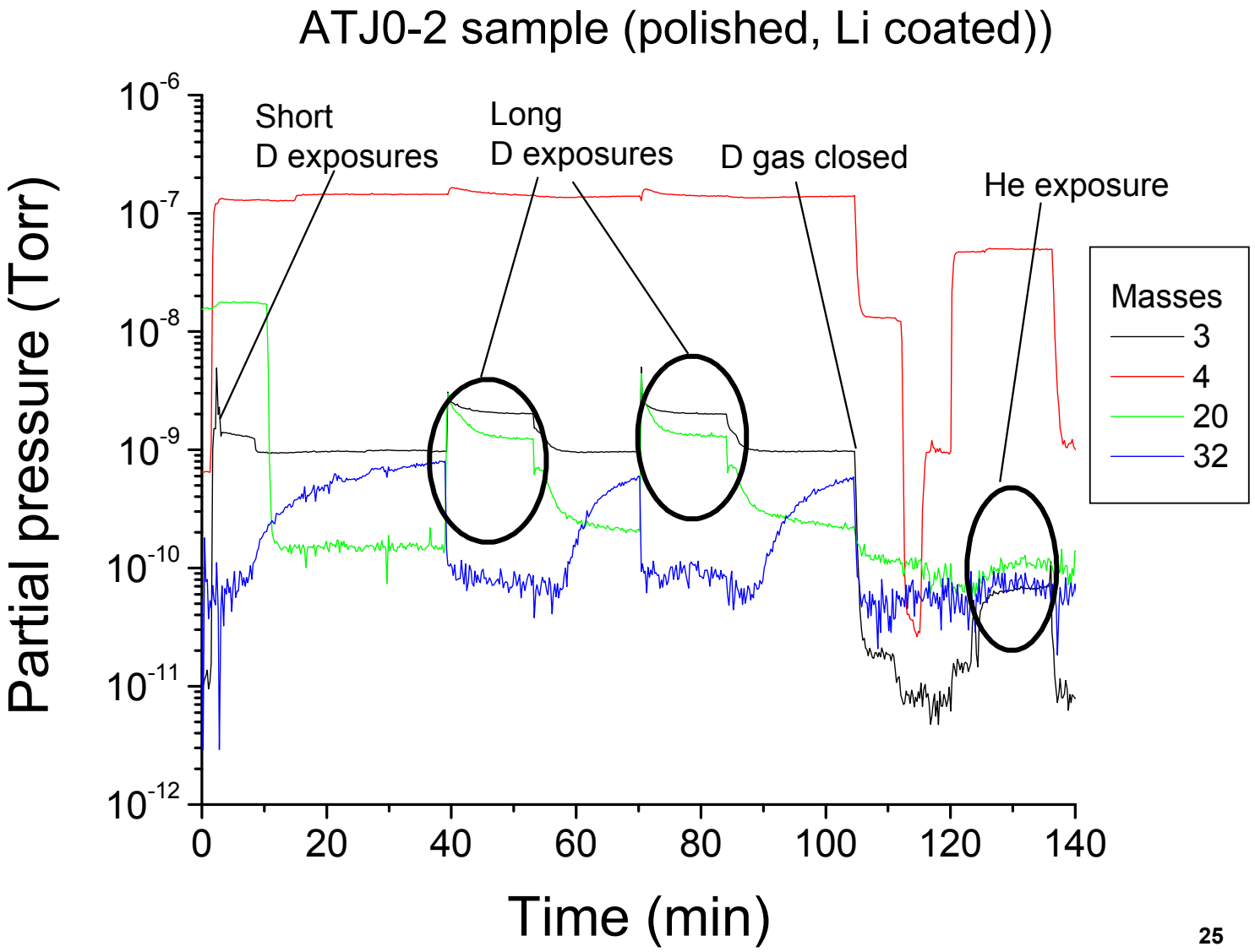
Evidence of D_2O formation



- Monitoring mass 20 closely shows two distinctive species
- Mass 32 is suppressed as soon as the D^+ beam is turned on (t = 9 min)
- Mass 20 has a sharp increase then exponentially reaches a steady state
- When D^+ is off, mass 20 decreases from steady state level, but not completely
- O_2 increase associated with the decrease in mass 20 suggests that it must be D_2O
- Same behavior found for 50 eV/amu case

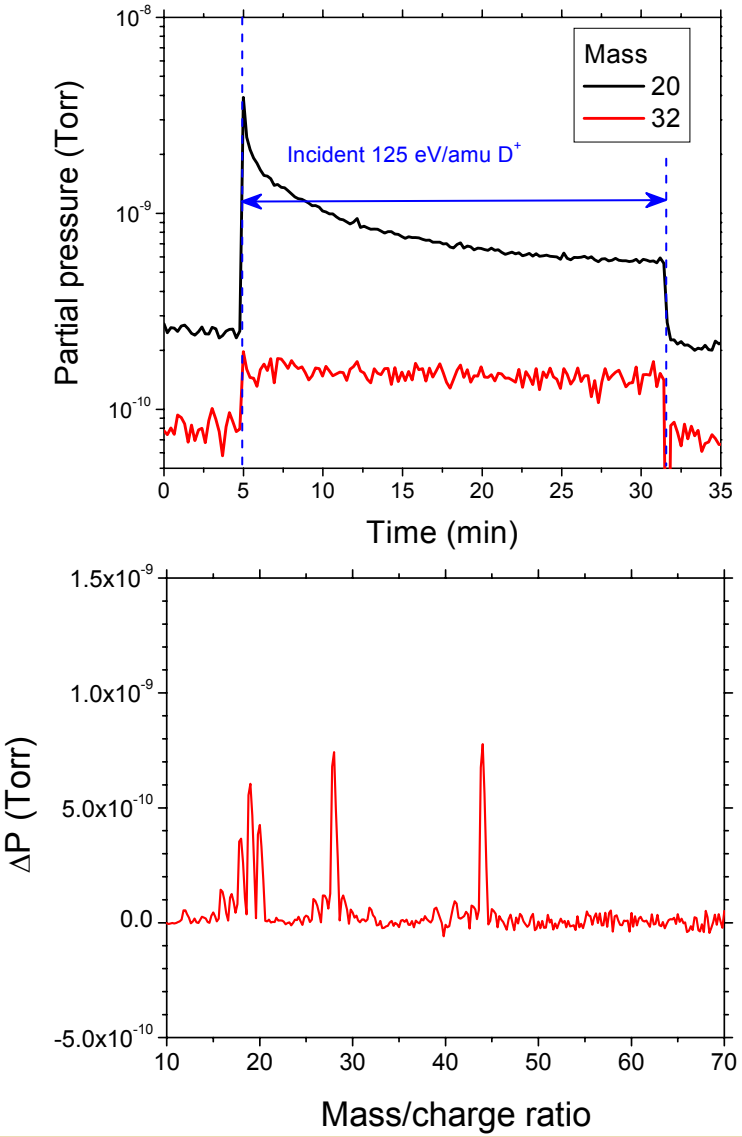
Chemistry at the Li surface

- Mass 32 evolves after D exposures
- D adsorption on Li/C surface currently being assessed
- D^+ exposure induces damage and HC emission is induced by kinetic ejection not thermal



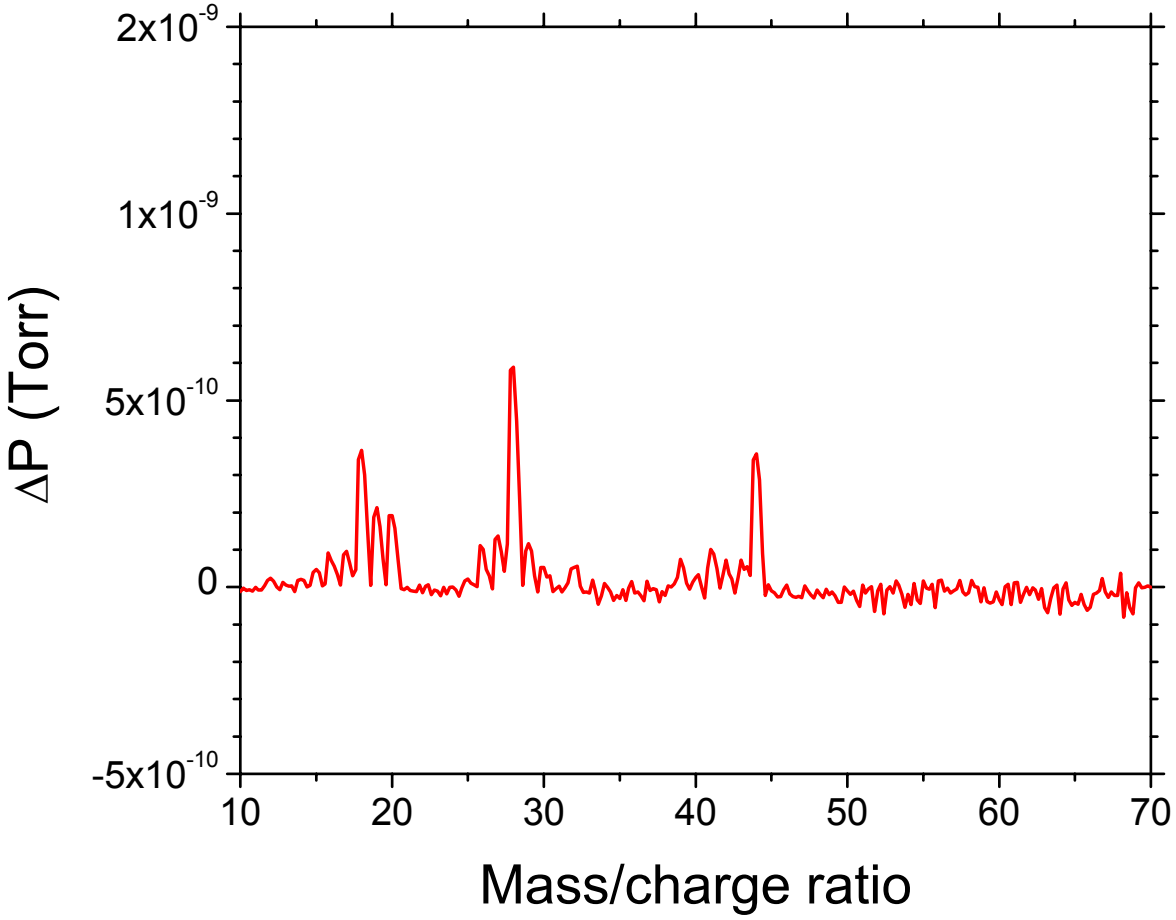
Li content on C surface goes down

- Sample ATJ0-2 was left overnight in chamber
- Another D^+ bombardment with 125 eV/amu was done
- This time, the mass 32 time-dependent emission from the lithiated graphite surface was not observed
- Could most of the Li have left the surface and gone into the bulk C overnight? Via intercalation processes?
- Previous experiments encourage that hypothesis
- Shifts in LEISS and AES peaks also suggest this.



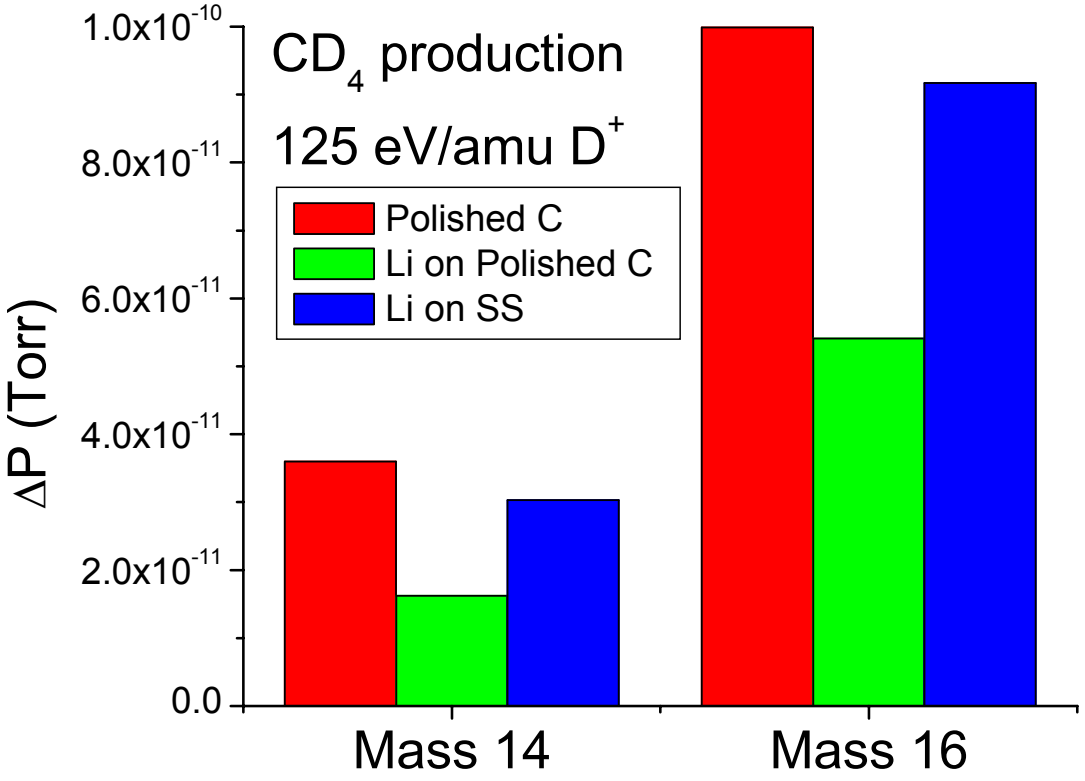
Experiments with Li on SS

- Some hydrocarbon production is observed for Li/SS
- Maybe C from steel? C and O measured on the Li/SS surface
- The behavior of mass 32 previously observed was not present in this experiment
- Future experiments need to be conducted for longer D^+ exposure times



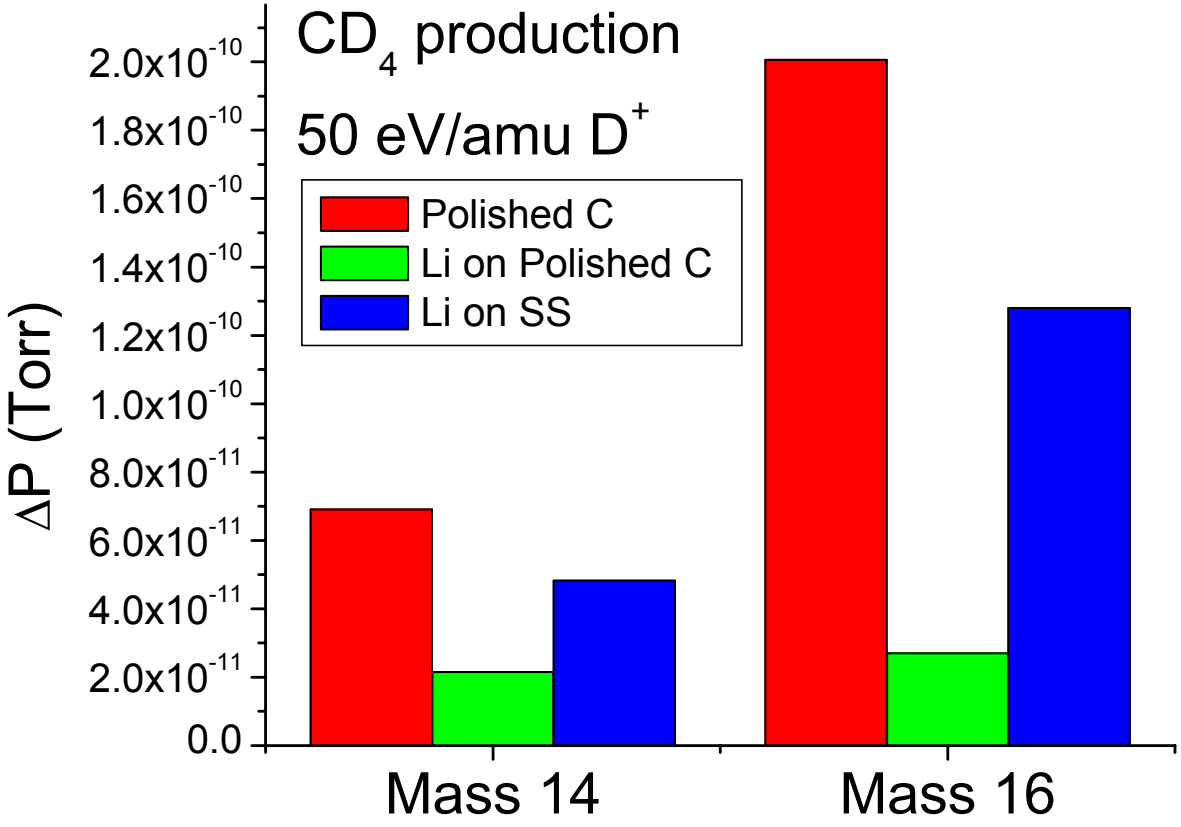
Comparison of CD_4 production

- **Masses 14 and 16 with least interference for CD_4 detection are best to assess methane formation and emission in Li/C system**
- **Relative intensities match CD_4 intensities (mass 14/mass 16 is ½, see table)**



Comparison of CD_4 production

- For the lower energy deposition, match on ratios not as good
- Formation of more hydrocarbons (consistent with Mech et al.)



Mechanisms at the Li/C surface

- Li/C surface is initially covered in oxygen and the dominant chemical state is Li oxide
- After the first short D irradiation, some of the implanted D reaches the surface and oxygen is released
- D bombardment induces damage breaking Li-O bonds leading to an exothermic reaction forming LiD, leaving free oxygen, which must recombine before release
- Suppression of D_2O release during the oxygen increase phase seems to indicate that the D remains bonded to the Li at the surface and oxygen surface combination is rate-limiting step
- As soon as irradiation stops, D starts migrating to the surface again and saturates the surface due to the D_2 partial pressure and also creates surface methyl groups that may prevent further D uptake and explain kinetic ejection of HCs at room temperature
- As soon as the D2 gas is removed, the Li surface can no longer be saturated with D and the Li gets covered by O again

Summary

- A complex mixed surface of Li/C/D has been diagnosed under D^+ bombardment at low-energy and room temp.
- Emission of hydrocarbon evolution qualitatively measured.
- Further work needed to quantify these mechanisms and understand the role of Li/C surfaces on D recycling properties
- Production of hydrocarbons at low-energy and room temperature are consistent with existing literature (Haasz, Roth,…). IMPACT provides a powerful facility for testing of mixed-material erosion
- On a lithiated graphitic surface oxygen and Li present, even on non-graphite surfaces
- Additional work will include: simultenous D and Li bombardment of Li/C surfaces, temperature-dependent data and assessment of erosion levels with QCM-DCU

Acknowledgements

- R. Bastasz and J. Whaley for providing ATJ graphite samples (with and w/o Li) and continuing collaborative effort
- R. Kaita, R. Majeski and H. Kugel for helpful discussions and feedback